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Dielectric properties of sodium fluoride added kaolinite at different firing temperatures

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Abstract

The dielectric properties of NaF doped and undoped kaolinite were measured as a function of frequency in the range 40 kHz to 50 MHz. The ε', $\tan\delta$ and σ_{ac} values are given as a function of firing temperature and NaF concentration. The addition of NaF increased the dielectric constant of pure kaolinite. However, the dielectric constant and ac conductivity of mullite obtained by the addition of NaF to kaolinite decreased from the value for pure kaolinite. Furthermore, the addition of NaF reduced the formation temperature of mullite from 1200 to 1000 °C.

Keywords: B. X-ray methods; C. Dielectric properties; D. Mullite; Kaolinite; NaF

1. Introduction

Ceramic substrates play an important role in high performance electronics. In recent years, logic devices with higher integration density, higher signal propagation rate, low dielectric constant and low thermal expansion coefficients have been developed [1,2]. In high density packaging, the important requirements are (a) thermal expansion match with silicon in order to reduce thermal stresses, (b) low dielectric constant to enhance signal processing and (c) high thermal conductivity for heat dissipation from the hard-driven integrated circuit devices [2].

Mullite not only has good high temperature properties but also has an excellent electrical insulating ability making it potentially useful in applications ranging from refractories to electronic substrates [3].

Although a number of papers have been published with regard to the application of mullite ceramics for substrates, most of them used mullite synthesized from different raw materials but not from clay [2]. Mullite is also formed after firing kaolinite at an elevated temperature. Primary mullite appears at a temperature around 1200 °C [4,5].

To synthesize mullite powders and to prepare dense sintered bodies involves high cost starting materials and processing techniques that makes them unsuitable for large scale commercial production. A cheaper alternative way involves use of raw materials like kaolinite, sillimanite, alumina, gibbsite and boehmite which have been frequent subjects of research [6,7]. The preparations of mullite ceramics from kaolinite was previously reported by others [4,7,8,9].

Many studies on the dielectric properties and electrical conductivity of minerals, clays and soils have been carried out in the recent years [10–17]. A number of dopants such as MgO, $Mg(NO_3)_2$, B_2O_3, Fe_2O_3, CeO_2, TiO_2 have been used. The dopants primarily aid reduction at the mullite formation temperature [15,18]. The alkaline treatment of clays which is used in acquiring mullite is a very rare research subject. Although there are a large number of reports on the conductivity of single alkali fluoride glasses, there are few reports on the electrical properties of fluoride glasses containing mixed alkali ions [19].

Relatively little attention has been given to determining the frequency dependence of electrical properties of better characterized ionic crystals which have very low defect concentration [20].

In this study, NaF with different concentrations was added to kaolinite for improving the dielectric properties of kaolinite and mullite which are used in electrical and electronics industries as

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circuit elements. It is aimed to determine the effect of NaF and firing temperature on the dielectric properties and formation of mullite. Dielectric properties of samples were measured at room temperature. Dielectric constants (ε'), loss tangents (tan δ) and alternating current (ac) conductivities (σ_{ac}) for pure kaolinite and doped kaolinite were calculated and given as a function of the frequency, firing temperature and concentration. Also, the dielectric properties and ac conductivity of mullite were evaluated. DTA, XRD and FTIR techniques were used to explain the structural changes and support the results.

2. Experimental

Kaolinite was mixed in distilled water and then NaF was added to give concentrations ranging from 0.05 to 50 mmol per 100 g kaolinite K: pure kaolinite; KNF1: 0.05 mmol NaF; KNF2: 0.5 mmol NaF; KNF3: 5 mmol NaF; KNF4 25 mmol NaF; KNF5: 50 mmol NaF. All the batches were wet mixed for 12 h, then mixed again with 2 wt% polyvinylalcohol (PVA) binder. The mixture was dried at 100 °C in air, then milled in an agate mortar. The test samples were prepared in disk form that was 30 mm diameter by 3 mm thickness.

The disks were placed on a mullite plate, loaded into a muffle furnace and fired at different temperatures for 21 h and then cooled to room temperature. Dielectric constants (ε') and loss tangents (tan δ) were measured using a circuit magnification meter type TF 1245 and TF 1246 oscilator (Marconi Instruments) in the frequency range 40 kHz and 50 MHz and room temperature. DTA analysis was done by Setaram TGA-DTA 92. Fourier transform infrared (FTIR) spectra of samples were measured using Perkin Elmer Spectrum One FTIR spectrometer by the KBr method. The X-ray powder diffraction (XRD) patterns were measured using a SHIMADZU XRD-6000 X-ray diffractometer with Cu Kα radiation.

3. Results and discussion

TG and DTG results are shown in Fig. 1. The weight loss occurs at three stages in the sample K; the first around 110 °C is due to removal of absorbed water, the second around 350 °C is due to burning of PVA and the third around 550 °C is due to removal of structural water from kaolinite. The DTA curves (Fig. 2) for kaolinite (K) and for NaF added and fired kaolinite (KNF3) give two endothermic and one exhothermic peaks due to loss of absorbed water, loss of structural water and burning of PVA, respectively.

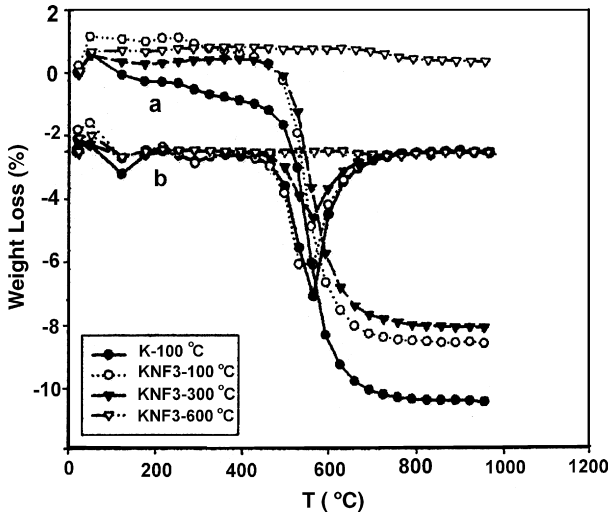

Fig. 1. Termograms of kaolinite and NaF added kaolinite (a) TG and (b) DTG.

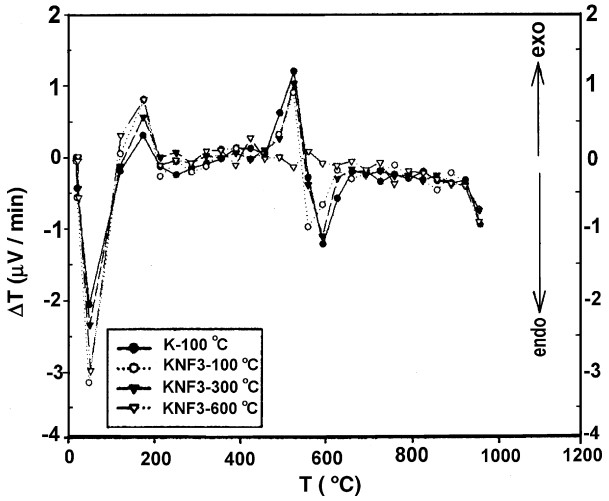

Fig. 2. DTA termogram of kaolinite and NaF added kaolinite.

The XRD patterns of KNF5 heat treated to different temperatures (300–1350 °C) are presented in Fig. 3. They clearly indicate that there is mullite in KNF5-1000 °C.

The FTIR spectrum of K given Fig. 4a agrees with refs. [16,17]. The spectra of the samples fired at 600, 800, 1000 and 1350 °C show a very broad similar band without much fine structure in the 400–1500 cm^{-1} range (Figs. 4 and 5). During the heat treatment, outer and inner hydroxyl groups remove. This is confirmed by the disappearance of the bands due to –OH groups in the sample at 600 °C and change in the nature of the doublet at 1000 and 1115 cm^{-1}. The shoulder appear at 1180 cm^{-1} at 800 °C and shifted to 1184 cm^{-1} at 1350 °C. This band is assigned to the asymmetric stretching vibration of the Si–O–Si network [21]. The bands at 1059 cm^{-1} at 600 °C and 1090 cm^{-1} at 1350 °C are assigned to the asymmetric stretching vibration of the Si–O–Al network. The shifting of these frequencies to higher wave numbers indicate the formation of mullite. This is supported by the XRD data (Fig. 3).

The dielectric constant of the kaolinite is 9 at 1 MHz. After adding PVA ($\varepsilon' = 2$ at 1 MHz) as a binder, the dielectric

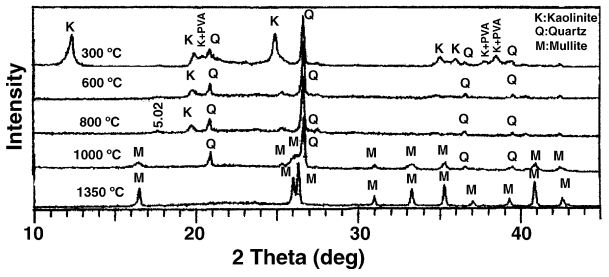

Fig. 3. XRD spectra for KNF5 at (a) 300 °C, (b) 600 °C, (c) 800 °C, (d) 1000 °C and (e) 1350 °C.

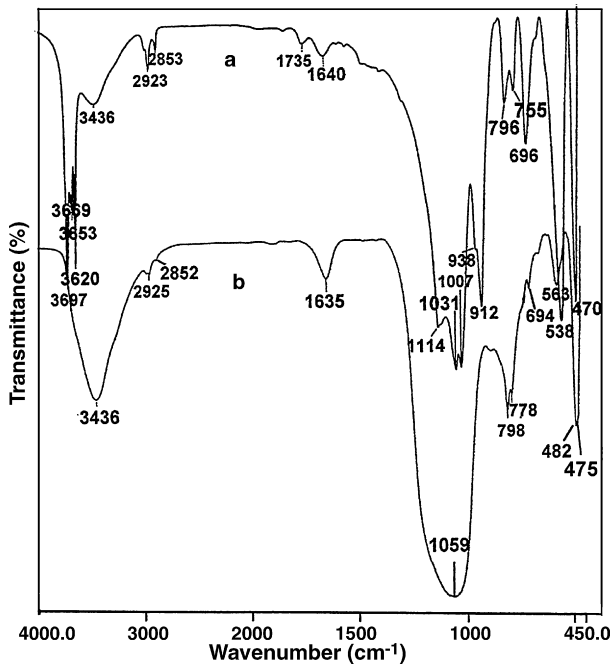

Fig. 4. FTIR spectrum of (a) kaolinite heated at 100 °C and (b) KNF5 sintered at 600 °C.

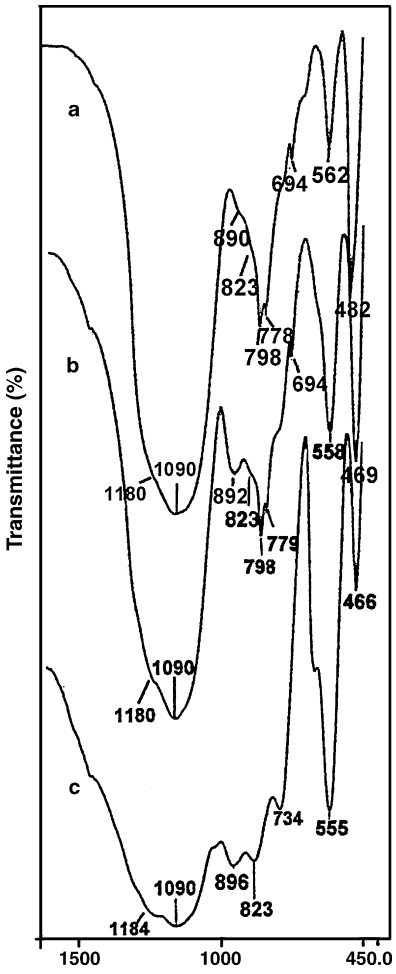

Fig. 5. FTIR spectrum of KNF5 sintered at (a) 800 °C, (b) 1000 °C and (c) 1350 °C.

constant of kaolinite decreases to approximately 6. The dielectric constant increases with increasing concentration of NaF ($\varepsilon' = 6$) and reaches 9.5 for KNF5 at 2 MHz. ε' values decrease regularly with increasing frequency (Fig. 6a). ε' values of the samples fired at 1350 °C do not change with frequency (Fig. 6b).

NaF is not effective and the dielectric constant values do not change at low concentrations (Fig. 7). At high NaF concentrations especially in the KNF5 sample, NaF starts mullitisation at 1000 °C. A similar lowering of mullitisation temperature has previously been reported for other materials such as MgO and WO_3 [3,22]. The beginning of mullitisation is observed by the raise to 3.8 in ε' values of the KNF5 sample. The ε' values of pure kaolinite and mullite are 10 and 6.5, respectively according to the refs. [6,11]. In this study the dielectric constant of kaolinite lowers from 9 to 4.3 and the dielectric constant of KNF5 lowers 9.5 to 3.7 during mullitisation.

The tan δ values of the all samples increase at all frequencies at 100 °C with increasing concentration of NaF and decrease regularly with rising frequency. The tan δ values of the samples fired at 1350 °C are not affected by concentration and frequency. The variation of other temperatures are plotted in Fig. 8.

The ac conductivities of pure kaolinite and samples of kaolinite with additive are calculated according to $\sigma = \omega\varepsilon_0\varepsilon' \tan\delta$ for all frequencies, concentrations and firing temperatures. The variation of ac conductivity with frequency for KNF1- KNF5 fired at 100 and 1350 °C are illustrated in Fig. 9a and b, respectively. The ac conductivity shows a small rise with concentration at all frequencies for all samples except for KNF5. The ac conductivities increase regularly with the rise in frequency for all samples. It has been shown that the Na^+ ions do not contribute to the conduction process and the charge carriers are only F^- ions [19,20,23].

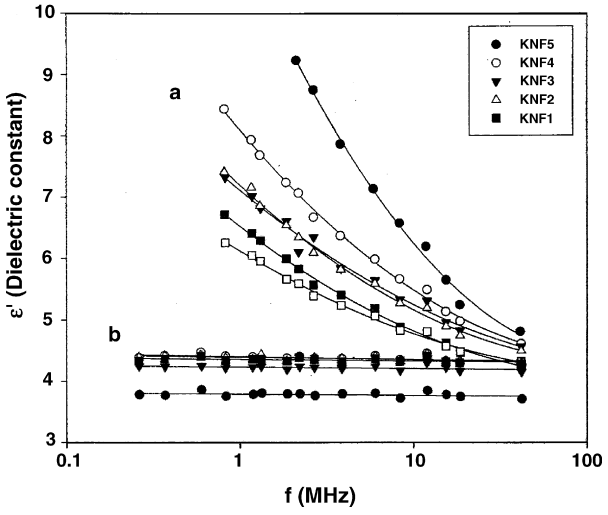

Fig. 6. Dependence of ε' on concentration and frequency (a) heated at 100 °C and (b) sintered at 1350 °C.

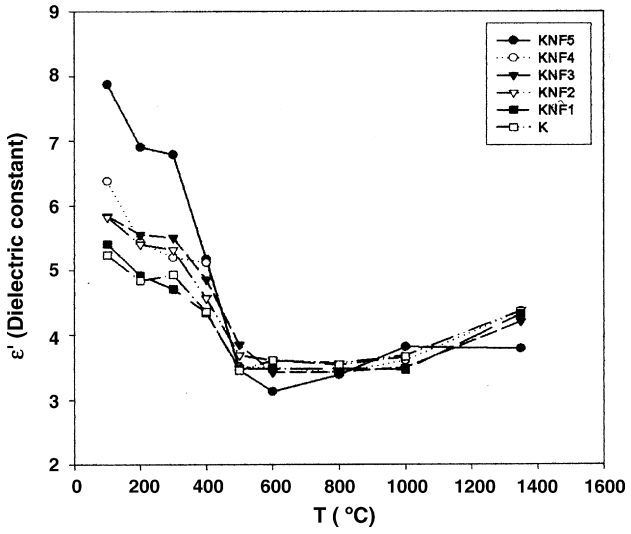

Fig. 7. Dependence of ε' on firing temperature and concentration at room temperature, for constant frequency ($f = 4$ MHz).

A glassy phase has been observed during mullite formation according to the results of X-ray analysis. If the amount of glassy phase was high, the mobilities of Na^+ ions would be greater and the conductivity would be higher [24,25]. As a result it can be seen from Fig. 9 that the ac conductivity can be lowered by firing and mullitisation. Even at low frequencies and high concentrations of NaF addition, conductivity can be much lower.

Fig. 10 gives the variation of the conductivity between 100 and 1350 °C at 4 MHz constant frequency. At 100 °C, the conductivity of the KNF1 sample is 29.2×10^{-4} Sm^{-1} while it reaches 121.8×10^{-4} Sm^{-1} for the KNF5 sample. The conductivity of KNF5 is the greatest below 500 °C. Above this temperature, it decreases. At all concentrations conductivity decreases with the increasing firing temperature and it shows slight variations above 500 °C.

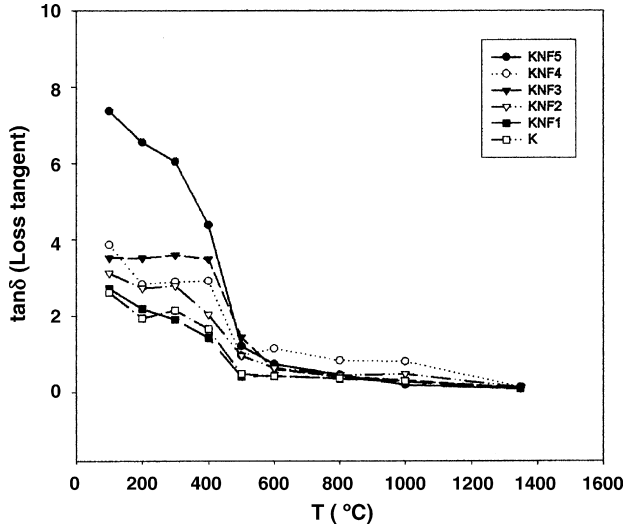

Fig. 8. Dependence of tan δ on firing temperature and concentration at room temperature, for constant frequency ($f = 4$ MHz).

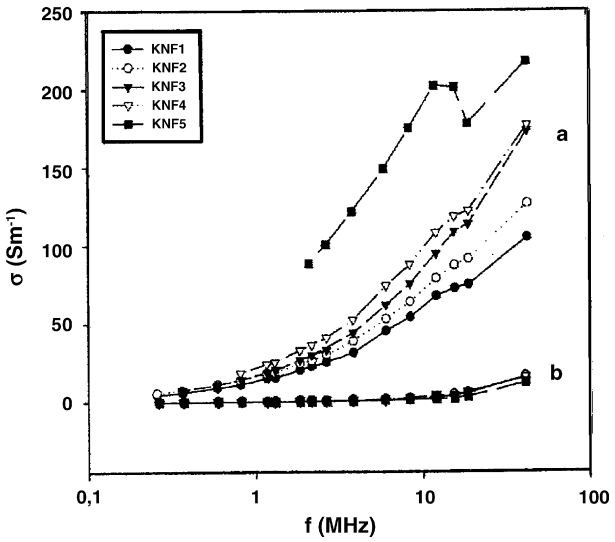

Fig. 9. Dependence of ac conductivity on concentration and frequency (a) heated at 100 °C and (b) sintered at 1350 °C.

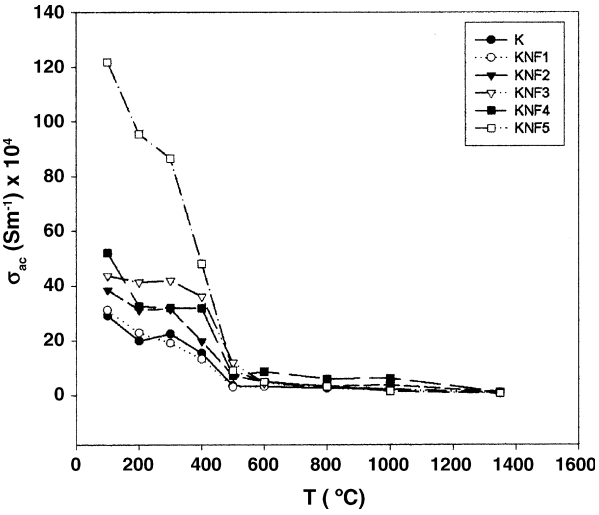

Fig. 10. Dependence of ac conductivity on firing temperature and concentration at room temperature, for constant frequency ($f = 4$ MHz).

4. Conclusions

The dielectric constant of pure kaolinite increases with increasing concentration of NaF and with firing temperature up to 500 °C. However, the dielectric constant of KNF5 decreases beginning from this temperature. Between 500 and 1000 °C, at low concentration, NaF is not effective and the dielectric constant values do not change.

Furthermore, the addition of NaF reduces the formation temperature of mullite from 1200 to 1000 °C. The dielectric constant and ac conductivity of mullite obtained by the addition of NaF to kaolinite decrease from the value for pure kaolinite. The dielectric constant of kaolinite decreases to 3.7 from 9 and tan δ reaches 0.1 from 7.5 at 1 MHz with the additon of NaF and the effect of firing temperature.

The dielectric constant of the fired samples at 1350 °C does not change with frequency.

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